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TITLE OF INVENTION : Aqueous Ink Recording Material

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REQUEST FOR EXAMINATION : None

[Abstract]

[Agenda] To provide an aqueous ink recording material, equipped with an ink-accepting layer having excellent ink absorbability, ink adhering property and water resistance, and does not cause the ink to bleed even when the amount of ink being attached per unit surface area has increased.

[Solution] An aqueous ink recording material, provided with an ink-accepting layer supported on a supporting member, comprising (I) polyvinyl acetal resin acquired by acetalizing polyvinyl alcohol with aromatic aldehyde and formaldehyde or acetaldehyde, (II) polyvinyl acetal resin acquired by acetalizing polyvinyl alcohol with acetaldehyde or butylaldehyde, and fine powder selected from silicic acid, silica, kaolin, clay, alumina, calcium carbonate, zeolite, titanium oxide, talc and porous spherical polymer.

Claims

[Claim 1] An aqueous ink recording material, that has an ink-accepting layer provided on a supporting member, where the ink-accepting layer is made of (I) a polyvinyl acetal resin acquired by acetalizing polyvinyl alcohol with aromatic aldehyde and at least one aldehyde selected from formaldehyde and acetaldehyde, (II) a polyvinyl acetal resin acquired by acetalizing polyvinyl alcohol with acetaldehyde or butylaldehyde, and at least a fine powder selected from a group comprising silicic acid, silica, kaolin, clay, alumina, calcium carbonate, zeolite, titanium oxide, talc and porous spherical polymer.

[Claim 2] The aqueous ink recording material according to Claim 1, where the polyvinyl acetal resin (I) is acquired by acetalizing polyvinyl alcohol with aromatic aldehyde and formaldehyde, and the degree of acetalization by aromatic aldehyde is 5 – 12 mol % and degree of acetalization by formaldehyde is 15 – 35 mol %.

[Claim 3] The aqueous ink recording material according to Claim 1, where the polyvinyl acetal resin (I) is acquired by acetalizing polyvinyl alcohol with aromatic aldehyde and acetaldehyde, and the degree of acetalization by aromatic aldehyde is 3 – 10 mol % and degree of acetalization by acetaldehyde is 10 – 30mol %.

[Claim 4] The aqueous ink recording material according to Claim 1, where the polyvinyl acetal resin (II) is acquired by acetalizing polyvinyl alcohol with acetaldehyde, and the degree of acetalization is 20 – 50 mol %.

[Claim 5] The aqueous ink recording material according to Claim 1, where the polyvinyl acetal resin (II) is acquired by acetalizing polyvinyl alcohol with butylaldehyde, and the degree of acetalization is 5 – 15 mol %.

[Claim 6] The aqueous ink recording material according to Claim 1, where the ratio of addition of the polyvinyl acetal resin (I) and the polyvinyl acetal resin (II) is 9/1 ~ 7/3, based on the weight ratio of the solid components.

Comprehensive explanation of invention

[0001]

[Technological field of invention]

This invention relates to aqueous ink recording material, and more particularly to aqueous ink recording material to be used favorably in the recording material that requires clearness of the image that is to be formed in full color.

[0002]

[Prior art]

Printer or plotter that employs inkjet recording process is widely used because they have low noise level, low running cost and cost of the main body, possibility of multicolor formation, have an ability to form a minute dot pattern, and thus can form a clearer image.

[0003]

Generally, following properties are required by the recording materials that are used in the inkjet recording system. (1) Excellent ink absorbability, and it must be able to absorb the ink dots adhered on the recording material quickly into the interior of the recording material. This condition is the most basic property that the recording material to be used in the inkjet recording process must have. Particularly, in case of the color inkjet recording process, often two or more ink dots may superimpose on the same spot on the surface of the recording material. As a result, the amount of ink being used per unit surface area increases. Therefore, the recording material must be able to absorb the ink dots into the interior of the recording material faster than when a monochromatic inkjet recording system is used.

[0004]

(2) It must be able to suppress spread of ink dots on the recording material. By preventing spread of the ink dots, it can cut off the connection among ink dots and increase the resolution and also raise the reflection density of the recorded material. And, in case of the color inkjet recording system, loss of clearness caused by mixing of colors due to interconnection of two or more ink dots having different colors can be prevented. As a result, spread of ink dots can be suppressed further.

[0005]

Beside the basic properties described in (1) and (2), following properties are required also.

(3) Ink-accepting layer of the recording material must be transparent. This is a necessary condition for the ink-accepting layer that is to be used in the sheet for overhead projector (OHP). Normally, the OHP sheet is made of a transparent sheet such as polyethylene terephthalate (PET) film and so on. PET film itself does not absorb water-soluble ink. Therefore, absorption of water-soluble ink is made possible by using PET film as the supporting member and an ink-accepting layer is provided on this supporting member. However, if this ink-accepting layer is opaque, it will shield off the light or scatter the light and thus it can not be used as an OHP sheet.

[0006]

(4) The recording material must have excellent water resistance. If the recording material has poor water resistance, adhesion of water or absorption of water may cause separation of the ink-accepting layer and thus the image may be lost.

[0007]

Traditionally, an ink-accepting layer made of a layer of water-soluble resin such as polyvinyl alcohol or polyvinyl pyrrolidone, provided on a supporting member such as plastic film, paper, or glass plate, is known as the aqueous ink recording material [Japanese Kokai Patent SHO 55-146786 (1980), Japanese Kokai Patent SHO 59-174311 (1984)].

[0008]

However, even though these recording materials may have acceptable water-soluble ink absorbability and fixability, they have a problem of insufficient water resistance of the ink-accepting layer. Due to this reason, for example, ~~Japanese Patent S140-87-107391 (1982)~~, discloses a technology relating to a recording material that has an ink-accepting layer made of a mixture of hydrophilic polymer and oleophilic polymer, to maintain a balance between the water absorbability and water resistance of the water-soluble ink.

[0009]

However, because the hydrophilic polymer and oleophilic polymer have poor mutual miscibility in these recording materials, the ink-accepting layer has insufficient transparency and therefore they could not be used as a OHP sheet.

[0010]

Thus, ~~Japanese Patent H1-5-23597 (1993)~~ discloses a technology that employs a water-resistant polyvinyl acetal resin such as polyvinylphenyl acetoacetal and so on.

[0011]

However, multicolor formation, fine dot formation, and high speed printing technology have seen a significant improvement in recent years. Particularly, the resolution has been improved from 360 dpi to about 720 dpi. Normally, black color is created by mixing cyan, yellow and magenta. In such case of color formation, the amount of ink being adhered per unit surface area increases drastically. Thus, if the recording material has low ink absorbability, bleeding (diffusion of ink) may occur on the surface of the recording layer or it may take a longer time to dry the ink. Therefore, the conventional recording materials described above do not have sufficient property, and further improvement in property is required.

[0012]

[Problems to be solved by invention]

In view of the above-described situation, the object of this invention is to provide an aqueous ink recording material that is equipped with an ink-accepting layer having excellent ink absorbability, ink fixability, and excellent water resistance, and does not cause bleeding of ink even when the amount of ink being adhered per unit surface area has increased.

[0013]

[Means to solve the invention]

This invention relates to an aqueous ink recording material that has an ink-accepting layer provided on the supporting member, where the ink-accepting layer is made of (I) a polyvinyl acetal resin acquired by acetalizing polyvinyl alcohol with aromatic aldehyde and either one of formaldehyde and acetaldehyde, (II) a polyvinyl acetal resin (II) acquired by acetalizing polyvinyl alcohol with acetaldehyde or butylaldehyde, and at least one kind of fine powder selected from a group comprising silicic acid, silica, kaolin,

clay, alumina, calcium carbonate, zeolite, titanium oxide, talc and porous spherical polymer. This invention is explained comprehensively in the following.

[0014]

The aqueous ink recording material of this invention is made by providing an ink-accepting layer on a supporting member. There is no particular restriction about the supporting member, and film or sheet made of synthetic resins such as polyesters, polystyrenes, polyvinylchlorides, polymethyl methacrylates, cellulose acetates, polyethylenes, or polycarbonates and so on; nonwoven clothes; fibers; clothes; papers; glass plate; board; or metallic plate and so on can be mentioned as the examples of such supporting member.

[0015]

The ink-accepting layer is made of polyvinyl acetal resin (I), polyvinyl acetal resin (II), and fine powder. The polyvinyl acetal resin (I) and polyvinyl acetal resin (II) can be obtained by acetalizing polyvinyl alcohol with aldehydes in the presence of an acid catalyst.

[0016]

Degree of polymerization of the preferred polyvinyl alcohol is 200 – 3500. If the degree of polymerization is lower than 200, it may be difficult to synthesize the polyvinyl alcohol. And, if it exceeds 3500, viscosity of its aqueous solution may be too high.

[0017]

Degree of saponification of the preferred polyvinyl alcohol is 75 – 99.8 mol %. If the degree of saponification is lower than 75 mol %, solubility in water will be poor. On the other hand, if it exceeds 99.8 mol %, it may be difficult to synthesize a modified polyvinyl alcohol.

[0018]

The polyvinyl acetal resin (I) can be prepared by acetalizing polyvinyl alcohol with aromatic aldehyde and either formaldehyde or acetaldehyde.

[0019]

There is no particular restriction about the aromatic aldehyde that can be used in this invention. Examples are benzaldehyde; alkyl-substituted benzaldehydes such as 2-methyl benzaldehyde, 3-methyl benzaldehyde, 4-methyl benzaldehyde and so on; halogen-substituted benzaldehydes; hydroxyl-substituted aromatic aldehydes such as p-hydroxy benzaldehyde, m-hydroxy benzaldehyde and so on; aromatic aldehydes that are substituted by alkoxy group, amino group, or cyano group and so on; and phenyl-substituted alkyl aldehydes such as phenyl acetaldehyde, β -phenyl propionaldehyde and so on.

[0020]

In order to raise its hydrophilic property, the aromatic aldehyde may have numerous hydroxyl groups or other polar groups. Generally, increasing the number of hydroxyl

group or other polar groups tends to change the hydrophilic property drastically. Because formaldehyde or acetaldehyde is used together in this invention, it can raise the water resistance of the entire ink-accepting layer without drastically changing its hydrophilic property.

[0021]

There is no particular restriction about the method of acetalization. Conventional methods such as dissolution method, precipitation method and proportionation method and so on can be mentioned as the examples of the method of acetalization. And, there is no particular restriction about the acid catalyst that can be used in this invention. Thus, inorganic acid such as hydrochloric acid, sulfuric acid or nitric acid and organic acid such as p-toluenesulfonic acid can be mentioned as the example.

[0022]

And, since, for example, the polyvinyl alcohol can be obtained easily by saponifying polyvinyl acetate, saponification and acetalization may be run concurrently by using polyvinylacetate instead of using polyvinyl alcohol.

[0023]

In case of acetalization by using aromatic aldehyde and formaldehyde to prepare the polyvinyl acetal resin (I), the degree of acetalization by the aromatic aldehyde is preferably 5 – 12 mol % and the degree of acetalization by formaldehyde is preferably 15 – 35 mol %. If the degree of acetalization by the aromatic aldehyde is lower than 5 mol %, water resistance may decrease, and if it exceeds 12 mol %, the water resistance may become excessive, resulting in lowering the ink absorbability and causing bleeding of ink during the printing work. And, if the degree of acetalization by formaldehyde is lower than 15 mol %, water resistance may decrease to the extent that lowers the effect of this invention. On the other hand, if it exceeds 35 mol %, water resistance may become excessive, resulting in lowering the ink absorbability and causing bleeding of ink during the printing work.

[0024]

And, if the polyvinyl acetal resin (I) is obtained by acetalizing with the aromatic aldehyde and acetaldehyde, preferred degree of acetalization by aromatic aldehyde is 3 – 10 mol % and preferred degree of acetalization by acetaldehyde is 10 – 30 mol %. If the degree of acetalization by aromatic aldehyde is lower than 3 mol %, water resistance may drop. And, if it exceeds 10 mol %, water resistance may become excessively high, and thus ink absorbability may drop and bleeding of ink may occur during the printing work. And, if the degree of acetalization by acetaldehyde is lower than 10 mol %, water resistance may drop to the extent that retards the effect of this invention. And, if it exceeds 30 mol %, water resistance will become excessively high, and it may lower the ink absorbability and cause the ink to bleed during the printing work.

[0025]

Polyvinyl acetal resin (II) can be obtained by acetalizing polyvinyl alcohol with acetaldehyde or butylaldehyde. If the polyvinyl acetal resin (II) is acetalized with

acetaldehyde, preferred degree of acetalization is 20 – 50 mol %. If the degree of acetalization by acetaldehyde is lower than 20 mol %, hydrophilic property will be excessively high and miscibility with the polyvinyl acetal resin (I) will become poorer. Thus, it will be difficult to form a uniform mixture. And, if it exceeds 50 mol %, hydrophobic property will become too high. As a result, it will be difficult to impart hydrophilic property to the extent of suppressing bleeding of ink.

[0026]

And, if the polyvinyl acetal resin (II) is acetalized with butylaldehyde, preferred degree of acetalization by butylaldehyde is 5 – 15 mol %. If the degree of acetalization by butylaldehyde is lower than 5 mol %, hydrophilic property will become too strong and miscibility with the polyvinyl acetal resin (I) will become poorer. As a result, it will be difficult to form a uniform mixture. And, if it exceeds 15 mol %, hydrophobic property will become too strong. Thus, it will be difficult to impart hydrophilic property to suppress the ink from bleeding.

[0027]

Preferred mixing ratio of the polyvinyl acetal resin (I) and the polyvinyl acetal resin (II) is 9/1 ~ 7/3, based on the weight ratio of its solid components. If the amount of polyvinyl acetal resin (I) relative to the amount of polyvinyl acetal resin (II) exceeds 9/1, water resistance will rise to the extent that causes the ink to bleed. And, if it is lower than 7/3, it may lower the water resistance. In case of adding polyvinyl acetal resin (I) and polyvinyl acetal resin (II), two or more polyvinyl acetal resins may be blended and used in the range that meets the above-said condition.

[0028]

In this invention, at least one fine powder selected from a group comprising silicic acid, silica, kaolin, clay, alumina, calcium carbonate, zeolite, titanium oxide, talc and porous spherical polymer is used as the fine power.

[0029]

There is no particular restriction about the type of porous spherical polymer. For example, polymethyl methacrylates, methyl methacrylate/ethyl methacrylate copolymers, polystyrene, polymethacrylate esters, polyacrylate esters, or sodium polyacrylate and so on can be used.

[0030]

Preferred average particle size of the fine powder is smaller than 0.05 μm . If it exceeds 0.05 μm , it can no longer capture the ink sufficiently and the clearness of the image may drop. Even more desirable average particle size is no larger than 0.02 μm .

[0031]

It is desirable that the content of fine powder in the ink-accepting layer is 0.3 – 20 g/m^2 . If it is less than 0.3 g/m^2 , effect of improvement of ink absorption and effect of prevention bleeding of ink caused by addition of the fine powder will not be sufficient.

On the other hand, if it exceeds 20 g/m^2 , hydrophilic property will become too strong and it may cause the ink to bleed.

[0032]

The aqueous ink recording material of this invention can be obtained by adding polyvinyl acetal resin (I), polyvinyl acetal resin (II), fine powder, and other additives (which will be mentioned later) as needed, to form an ink-accepting layer on a supporting member. Specifically, for example, after adding and mixing the fine powder thoroughly with the solution of polyvinyl acetal resin (I) and polyvinyl acetal resin (II), this aqueous solution is coated on the supporting member by using an appropriate method such as by roll coater method or blade coater method and so on, and finally the coated layer is dried, to obtain the aqueous ink recording material of this invention.

[0033]

It is desirable that the ink-accepting layer is coated on a supporting member so that its dry weight will be $0.5 - 30 \text{ g/m}^2$. If it is less than 0.5 g/m^2 , the amount of ink being absorbed may not be sufficient and the ink may bleed. On the other hand, if it exceeds 30 g/m^2 , moisture absorbability in high humidity environment will be too high, water resistance may drop, and the recording material may curl.

[0034]

Variety of known additives may be added in the ink-accepting layer as needed, as long as it does not interfere with the object of this invention. For example, waterproofing agent such as polyamide resin, melamine/formaldehyde resin, or glyoxal may be added to raise its water resistance. And, glycerin, ethyleneglycol, polyethyleneglycol, surface active agent, UV absorber, pigment dispersing agent, antifoam, preservative, and/or pH regulating agent may be added to raise the ink adsorbability.

[0035]

And, surface of the supporting member may be oxidized ahead of time with corona discharge or an adhesive resin may be provided on the supporting member to improve the bondability of the supporting member and the ink-accepting layer.

[0036]

There is no particular restriction about the aqueous ink that can be used in the aqueous ink recording material of this invention. Aqueous inks that contain water-soluble dyes, water, water-miscible organic solvent, wetting agent, dye-solubilizing agent, antifungal agent and so on, described in Japanese Kokai Patent SHO 49-2105 (1974), Japanese Kokai Patent SHO 49-395K1 (1974), Japanese Kokai Patent SHO 49-9620 (1974), Japanese Kokai Patent SHO 50-123002 (1975), and so on, for example, can be used. may be used appropriately.

[0037]

In case of printing, the ink in the aqueous ink recording material of this invention can be absorbed quickly to the extent that prevents it effectively from spreading, even when a large amount of ink is used per unit surface area, because ink absorbability has been

increased by adding the polyvinyl acetal resin (II) that has hydrophilic property, prepared by acetalizing with acetaldehyde or butylaldehyde, to the polyvinyl acetal resin (I) that has hydrophobic property, prepared by acetalizing with aromatic aldehyde and formaldehyde or acetaldehyde.

[0038]

Thus, because hydrophilic polyvinyl acetal resin (II) exists in the ink-accepting layer, the aqueous ink can easily enter the interior of the ink-accepting layer. On the other hand, the hydrophobic polyvinyl acetal resin (I) increases the water-resistance of the ink-accepting layer. Because the polyvinyl acetal resin (I) and the polyvinyl acetal resin (II) have its own degrees of acetalization, it can further increase the ink absorbability and improve also the water resistance. And, because the polyvinyl acetal resin (I) and the polyvinyl acetal resin (II) are added at a certain specific ratio, it balances well the ink absorbability and water resistance.

[0039]

[Examples]

This invention is explained further by way of the following examples which, however, are not intended to limit the scope of this invention.

[0040]

Example 1

[Preparation of polyvinyl acetal resin (I)]

Polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 88 mol %) 200 g was added in pure water 1600 g, and it was dissolved by agitating at 90°C for about 2 hours, to prepare a solution. The thus-obtained solution was cooled to 45°C, and then hydrochloric acid (concentration = 35 weight %) 50 g was added to this solution, and it was cooled down to 20°C. Then, benzaldehyde 15 g and formaldehyde 30 g were added to this solution, and acetalization reaction was carried out at 25°C for 4 hours (degree of acetalization by benzaldehyde = 5 mol %, degree of acetalization by acetaldehyde = 20 mol %). Subsequently, the liquid temperature was lowered to 20°C. While being agitated, aqueous sodium hydroxide solution (concentration = 10 weight %) 192 g was added to neutralize the reaction mixture, and thus a sponge-like precipitate was obtained. This sponge-like precipitate was washed with water to remove the neutral salt and non-reacted aldehydes, and then it was dried, to obtain a powder of polyvinyl acetal resin.

[0041]

[Preparation of polyvinyl acetal resin (II)]

Polyvinyl alcohol (degree of polymerization = 600600, degree of saponification = 88 mol %) 200 g was added in pure water 1600 g, and it was dissolved by agitating at 90°C for about 24 hours, to prepare a solution. The thus-obtained solution was cooled down to 45°C, and then hydrochloric acid (concentration = 50 weight %) 50 g was added, and then it was cooled down to 35°C. Then, acetaldehyde 67 g was added to run acetalization reaction at 35±C for 3 hours (degree of acetalization by acetaldehyde = 31 mol %). Subsequently, temperature of the reaction mixture was lowered down to 20°C,

and aqueous NaOH solution (concentration = 10 weight %) 192 g was added with agitation to neutralize the reaction mixture. Thus a clear solution was obtained.

[0042]

[Preparation of aqueous ink recording material]

The thus-obtained polyvinyl acetal resin (I) was dissolved in a solvent mixture containing water and ethanol at weight ratio = 1 : 1. Subsequently, polyvinyl acetal resin (II) was added in such a way that the mixing ratio of the polyvinyl acetal resin (I) and the polyvinyl acetal resin (II) would be 8 : 2 (ratio, based on the weight of components) and they were mixed thoroughly. Then, fine powder of silicic acid (average particle size = 0.02 μm) was added and they were mixed thoroughly. This material was coated on a PET film (thickness = 100 μm) so that the dry weight would be 12 g/m^2 , to form an ink-accepting layer. Incidentally, weight of the fine powder of silicic acid being added was 6 g/m^2 .

[0043]

[Evaluation of the aqueous ink recording material]

Color inks were printed by flat coating technique (in the order of cyan \rightarrow magenta \rightarrow cyan \rightarrow yellow \rightarrow magenta) on the aqueous ink recording material in the same 3 x 3 cm square area by using a commercial inkjet printer (a type that can create black color by mixing cyan, yellow and magenta colors), and water resistance and bleeding of inks from the image area were evaluated by the following procedures. Results are shown in Table 1.

[0044]

(1) Water resistance :

Twenty four hours after printing, the material having a flat-coated image area (3 x 3 cm square area) was dipped in tap water for 1 minute, and then it was lifted from water. Condition of the image area was examined by naked eyes. Results are expressed, based on the following judgement criteria.

Excellent	: Condition of the image did not change
Good	: Swollen. However, after water has dried off, it returned to the original condition
Fair	: A portion of the ink has leached out and the ink-accepting layer has swollen
Poor	: The ink-accepting layer has dissolved and has been washed away

[0045]

(2) Bleeding of ink (ink diffusion) :

Twenty four hours after printing, condition (obscureness of the edge of the image area) of the flat-coated image area (3 x 3 cm square) was examined by naked eyes. Results are expressed, based on the following judgement criteria.

- ⊙ : Size of diffusion from the edge of the image area was less than 50 μm
- : Size of diffusion from the edge of the image area was less than 100 μm
- △ : Size of diffusion from the edge of the image area was less than 300 μm
- x : Size of diffusion from the edge of the image area was larger than 300 μm

[0046]

Incidentally, size of diffusion means the lengthwise size of the maximum diffusion toward the outside from the edge of the intended printed image area.

[0047]

Example 2

Polyvinyl acetal resin (I) was prepared by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 98 mol %) and setting the degree of acetalization by benzaldehyde at 7 mol % and setting the degree of acetalization by acetaldehyde at 15 mol %. And, polyvinyl acetal resin (II) was prepared also by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 1000, degree of saponification = 98 mol %) and setting the degree of acetalization by acetaldehyde at 45 mol %. Aqueous ink recording material was prepared by the procedure of Example 1, except mixing the thus-obtained polyvinyl acetal resin (I) and polyvinyl acetal resin (II) at a weight ratio (as solids) of 8 : 2, and then adding a fine powder of alumina (average particle size = 0.01 μm). It was evaluated like Example 1, and results are presented in Table 1.

[0048]

Example 3

Polyvinyl acetal resin (I) was prepared by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 800, degree of saponification = 88 mol %) and setting the degree of acetalization by benzaldehyde at 6 mol % and setting the degree of acetalization by acetaldehyde at 25 mol %. And, polyvinyl acetal resin (II) was prepared also by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 2000, degree of saponification = 88 mol %) and setting the degree of acetalization by acetaldehyde at 25 mol %. And, an aqueous ink recording material was prepared by the procedure of Example, except mixing the thus-obtained polyvinyl acetal resin (I) and polyvinyl acetal resin (II) at a weight ratio of 8 : 2 (as solids) and then adding porous spherical polymethyl methacrylate particles (average particle size = 0.05 μm), and it was evaluated by the procedure of Example 1. Results are presented in Table 1.

[0049]

Example 4

Polyvinyl acetal resin (I) was prepared by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 88 mol %) and setting the degree of acetalization by benzaldehyde at 5 mol % and setting the degree of acetalization by acetaldehyde at 20 mol %. And, polyvinyl acetal resin (II) was prepared also by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 600, degree of saponification = 88 mol %) and setting the degree of acetalization by butylaldehyde at 9 mol %. An aqueous ink recording material

was prepared by the procedure of Example 1, except mixing the thus-obtained polyvinyl acetal resin (I) and polyvinyl acetal resin (II) at a weight ratio of 8 : 2 (based on solids) and then adding a fine powder of silicic acid (average particle size = 0.02 μm). It was evaluated by the procedure of Example 1. Results are presented in Table 1.

[0050]

Example 5

Polyvinyl acetal resin (I) was prepared by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 98 mol %) and setting the degree of acetalization by benzaldehyde at 7 mol % and the degree of acetalization by acetaldehyde at 15 mol %. An aqueous ink recording material was prepared also by the procedure of Example 1, except mixing the thus-obtained polyvinyl acetal resin (I) and the polyvinyl acetal resin (II) at a weight ratio of 8 : 2 (based on solids) and then adding a fine powder of alumina (average particle size = 0.01 μm). It was evaluated by the procedure of Example 1, and results are presented in Table 1.

[0051]

Example 6

Polyvinyl acetal resin (I) was prepared by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 800, degree of saponification = 88 mol %) and setting the degree of acetalization by benzaldehyde at 6 mol % and the degree of acetalization by acetaldehyde at 25 mol %. Polyvinyl acetal resin (II) was prepared also by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 2000, degree of saponification = 88 mol %) and setting the degree of acetalization by butylaldehyde at 6 mol %. An aqueous ink recording material was prepared by the procedure of Example 1, except mixing the thus-obtained polyvinyl acetal resin (I) and polyvinyl acetal resin (II) at a weight ratio of 8 : 2 (based on solids) and then adding a porous spherical polymethyl methacrylate particles (average particle size = 0.05 μm). It was evaluated by the procedure of Example 1, and results are presented in Table 1.

[0052]

Example 7

Polyvinyl acetal resin (I) was prepared by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 88 mol %) and setting the degree of acetalization by benzaldehyde at 7 mol % and setting the degree of acetalization by formaldehyde at 20 mol %. Polyvinyl acetal resin (II) was prepared also by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 600, degree of saponification = 88 mol %) and setting the degree of acetalization by acetaldehyde at 31 mol %. An aqueous ink recording material was prepared by the procedure of Example 1, except mixing the thus-obtained polyvinyl acetal resin (I) and polyvinyl acetal resin (II) at a weight ratio of 8 : 2 (based on solids) and then adding a fine powder of silicic acid (average particle size = 0.02 μ). It was evaluated by the procedure of Example 1, and results are presented in Table 1.

[0053]

Example 8

Polyvinyl acetal resin (I) was prepared by the procedure of Example 1, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 98 mol %) and setting the degree of acetalization by benzaldehyde at 9 mol % and setting the degree of acetalization by formaldehyde at 25 mol %. And, polyvinyl acetal resin (II) was prepared also by the procedure of Example 1 also, except using a polyvinyl alcohol (degree of polymerization = 1000, degree of saponification = 98 mol %) and setting the degree of acetalization by acetaldehyde at 45 mol %. An aqueous ink recording material was prepared by the procedure of Example 1, except mixing the thus-obtained polyvinyl acetal resin (I) and polyvinyl acetal resin (II) at a weight ratio of 8 : 2 (based on solids) and then adding a fine powder of alumina (average particle size = 0.01 μm). It was evaluated by the procedure of Example 1, and results are presented in Table 1.

[0054]

Example 9

Polyvinyl acetal resin (I) was prepared like Example 1, except using a polyvinyl alcohol (degree of polymerization = 800, degree of saponification = 88 mol %) and setting the degree of acetalization by benzaldehyde at 7 mol % and setting the degree of acetalization by formaldehyde at 16 mol %. And, polyacetal resin (II) was prepared also like Example 1, except using a polyvinyl alcohol (degree of polymerization = 2000, degree of saponification = 88 mol %) and setting the degree of acetalization by acetaldehyde at 25 mol %. An aqueous ink recording material was prepared like Example 1, except mixing the thus-obtained polyvinyl acetal resin (I) and polyvinyl acetal resin (II) at a weight ratio of 8 : 2 (based on solids) and then adding a porous spherical polymethyl methacrylate particles (average particle size = 0.05 μm). It was evaluated like Example 1, and results are presented in Table 1.

[0055]

Example 10

Polyvinyl acetal resin (I) was prepared like Example 1, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 88 mol %) and setting the degree of acetalization by benzaldehyde at 7 mol % and setting the degree of acetalization by formaldehyde at 20 mol %. And, polyvinyl acetal resin (II) was prepared also like Example 1, except using a polyvinyl alcohol (degree of polymerization = 600, degree of saponification = 88 mol %) and setting the degree of acetalization by butylaldehyde at 9 mol %. An aqueous ink recording material was prepared like Example 1, except mixing the thus-obtained polyvinyl acetal resin (I) and polyvinyl acetal resin (II) at a weight ratio of 8 : 2 (based on solids) and then adding a fine powder of silicic acid (average particle size = 0.02 μm). It was evaluated like Example 1, and results are presented in Table 1.

[0056]

Example 11

Polyvinyl acetal resin (I) was prepared like Example 1, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 98 mol %) and

setting the degree of acetalization by benzaldehyde at 9 mol % and setting the degree of acetalization by formaldehyde at 25 mol %. And, polyvinyl acetal resin (II) was prepared also like Example 1, except using a polyvinyl alcohol (degree of polymerization = 1000, degree of saponification = 98 mol %). An aqueous ink recording material was prepared like Example 1, except mixing the thus-obtained polyvinyl acetal resin (I) and polyvinyl acetal resin (II) at a weight ratio of 8 : 2 (based on solids) and then adding a fine powder of alumina (average particle size = 0.01 μm). It was evaluated like Example 1, and results are presented in Table 1.

[0057]

Example 12

Polyvinyl acetal resin (I) was prepared like Example 1, except using a polyvinyl alcohol (degree of polymerization = 800, degree of saponification = 88 mol %) and setting the degree of acetalization by benzaldehyde at 7 mol % and setting the degree of acetalization by formaldehyde at 16 mol %. Polyvinyl acetal resin (II) was prepared also like Example 1, excepting using a polyvinyl alcohol (degree of polymerization = 2000, degree of saponification = 88 mol %) and setting the degree of acetalization by butylalcohol at 6 mol %. An aqueous ink recording material was prepared like Example 1, except mixing the thus-obtained polyvinyl acetal resin (I) and polyvinyl acetal resin (II) at a weight ratio of 8 : 2 (based on solids) and then adding a porous spherical polymethyl methacrylate particles (average particle size = 0.05 μm). It was evaluated like Example 1, and results are presented in Table 1.

[0058]

Comparative Example 1

An aqueous ink recording material was prepared like Example 1, except using the polyvinyl acetal resin (I) of the Example 1, without adding the polyvinyl acetal resin (II), and then adding a fine powder of silicic acid (average particle size = 0.02 μm). It was evaluated like Example 1, and results are presented in Table 2.

[0059]

Comparative Example 2

An aqueous ink recording material was prepared like Example 7, except using the polyvinyl acetal resin (I) of the Example 7, without adding the polyvinyl acetal resin (II), and then adding a fine powder of silicic acid (average particle size = 0.02 μm). It was then evaluated, and results are presentend in Table 2.

[0060]

Comparative Example 3

Polyvinyl acetal resin (I) was prepared like Example 1, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 88 mol %), running acetalization with benzaldehyde alone without using acetaldehyde, and setting the degree of acetalization by benzaldehyde at 9 mol %. Polyvinyl acetal resin (II) was not prepared. Then, an aqueous ink recording material was prepared like Example 1 by using only the thus-obtained polyvinyl acetal resin (I) and then adding a fine powder of

silicic acid (average particle size = 0.02 μm). It was evaluated like Example 1, and results are presented in Table 2.

[0061]

Comparative Example 4

Polyvinyl acetal resin (I) was prepared like Example 2, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 98 mol %), and running acetalization with benzaldehyde alone without acetaldehyde and setting the degree of acetalization by benzaldehyde at 12 mol %. Polyvinyl acetal resin (II) was not prepared. An aqueous ink recording material was prepared like Example 1, by using polyvinyl acetal resin (I) alone and adding a fine powder of alumina (average particle size = 0.01 μm). It was evaluated like Example 1, and results are presented in Table 2.

[0062]

Comparative Example 5

Polyvinyl acetal resin (I) was prepared like Example 1, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 88 mol %), running the acetalization reaction with acetaldehyde without using aromatic aldehyde, and setting the degree of acetalization by acetaldehyde at 20 mol %. Polyvinyl acetal resin (II) was not prepared. An aqueous ink recording material was prepared like Example 1, by adding a fine powder of silicic acid (average particle size = 0.02 μm) to the polyvinyl acetal resin (I), and it was evaluated. Results are presented in Table 2.

[0063]

Comparative Example 6

Polyvinyl acetal resin (I) was prepared like Example 1, except using a polyvinyl alcohol (degree of polymerization = 1700, degree of saponification = 98 mol %), using acetaldehyde alone to run the acetalization without using aromatic aldehyde, and setting the degree of acetalization by acetaldehyde at 50 mol %. Polyvinyl acetal resin (II) was not prepared. An aqueous ink recording material was prepared like Example 2, by adding a fine powder of alumina (average particle size = 0.01 μm) to the polyvinyl acetal resin (I), and it was evaluated. Results are presented in Table 2.

[0064]

Comparative Example 7

Polyvinyl acetal resin (I) was prepared like Example 1, except using a polyvinyl alcohol (degree of polymerization = 600, degree of saponification = 88 mol %), using butylaldehyde alone to run the acetalization reaction without using aromatic aldehyde, and setting the degree of acetalization by butylaldehyde at 9 mol %. Polyvinyl acetal resin (II) was not prepared. An aqueous ink recording material was prepared like Example 4, by adding a fine powder of silicic acid (average particle size = 0.02 μm) to the polyvinyl acetal resin (I), and it was evaluated. Results are presented in Table 2.

[0065]

Comparative Example 8

Polyvinyl acetal resin (I) was prepared like Example 1, except using a polyvinyl alcohol (degree of polymerization = 1000, degree of saponification = 98 mol %), using butylaldehyde alone to run the acetalization reaction without using aromatic aldehyde, and setting the degree of acetalization by butylaldehyde at 15 mol %. Polyvinyl acetal resin (II) was not prepared. An aqueous ink recording material was prepared like Example 5, by adding a fine powder of alumina (average particle size = 0.01 μm) to the polyvinyl acetal resin (I), and it was evaluated. Results are presented in Table 2.

[0066]

Comparative Example 9

An aqueous ink recording material was prepared like Example 1, except omitting the fine powder of silicic acid (dry weight of the ink-accepting layer was 12 g/m^2), and it was evaluated like Example 1. Results are presented in Table 2.

[0067]

Comparative Example 10

An aqueous ink recording material was prepared like Example 4, except omitting the powder of silicic acid (dry weight of ink-accepting layer was 12 g/m^2), and it was evaluated like Example 1. Results are presented in Table 2.

[0068]

Comparative Example 11

An aqueous ink recording material was prepared like Example 7, except omitting the fine powder of silicic acid (dry weight of ink-accepting layer was 12 g/m^2) and it was evaluated like Example 1. Results are presented in Table 2.

[0069]

Comparative Example 12

An aqueous ink recording material was prepared like Example 10, except omitting the fine powder of silicic acid (dry weight of ink-accepting layer was 12 g/m^2), and it was evaluated like Example 1. Results are presented in Table 2.

[0070]
[Table 1]

Aqueous ink-accepting layer												Properties of recording material			
Polyvinyl alcohol resin (I)												(I)/(II) mixing ratio	Water resistance	Ink diffusion	Transparency
Polyvinyl alcohol		Aromatic aldehyde		Aldehyde		Polyvinyl alcohol resin (II)									
d.p.*	d.s.** (mol %)	d.s.** (mol %)	Benzaldehyde	d.s.** (mol %)	Acetaldehyde	d.p.*	d.s.** (mol %)	d.s.** (mol %)	Acetaldehyde						
1700	88	88	(5)	(7)	(20)	600	88	(31)	(45)						
1	1700	88	Benzaldehyde	Benzaldehyde	Acetaldehyde	600	88	Acetaldehyde	Acetaldehyde	8/2	Excellent	○	○		
2	1700	98	Benzaldehyde	Benzaldehyde	Acetaldehyde	1000	98	Acetaldehyde	Acetaldehyde	8/2	Excellent	○	○		
3	800	88	Benzaldehyde	Benzaldehyde	Acetaldehyde	2000	88	Acetaldehyde	Acetaldehyde	8/2	Excellent	○	○		
4	1700	88	Benzaldehyde	Benzaldehyde	Acetaldehyde	600	88	Benzaldehyde	Benzaldehyde	8/2	Excellent	○	○		
5	1700	98	Benzaldehyde	Benzaldehyde	Acetaldehyde	1000	98	Benzaldehyde	Benzaldehyde	8/2	Excellent	○	○		
6	800	88	Benzaldehyde	Benzaldehyde	Acetaldehyde	2000	88	Benzaldehyde	Benzaldehyde	8/2	Excellent	○	○		
7	1700	88	Benzaldehyde	Benzaldehyde	Formaldehyde	600	88	Acetaldehyde	Acetaldehyde	8/2	Excellent	○	○		
8	1700	98	Benzaldehyde	Benzaldehyde	Formaldehyde	1000	98	Acetaldehyde	Acetaldehyde	8/2	Excellent	○	○		
9	800	88	Benzaldehyde	Benzaldehyde	Formaldehyde	2000	88	Acetaldehyde	Acetaldehyde	8/2	Excellent	○	○		
10	1700	88	Benzaldehyde	Benzaldehyde	Formaldehyde	600	88	Benzaldehyde	Benzaldehyde	8/2	Excellent	○	○		
11	1700	98	Benzaldehyde	Benzaldehyde	Formaldehyde	1000	98	Benzaldehyde	Benzaldehyde	8/2	Excellent	○	○		
12	800	88	Benzaldehyde	Benzaldehyde	Formaldehyde	2000	88	Benzaldehyde	Benzaldehyde	8/2	Excellent	○	○		

* d.p. : Degree of polymerization ; ** d.s. : Degree of saponification ; *** d.s. : Degree of acetalization

[0071]
[Table 2]

Aqueous ink-accepting layer												Properties of recording material					
	Polyvinyl alcohol			Polyvinyl acetal resin (I)		Polyvinyl acetal resin (II)			(I)/(II) mixing ratio	Fine powder (particle size : μm)	Water resistance	Ink diffusion	Transparency				
	Aromatic aldehyde			Aldehyde			Polyvinyl alcohol										
	d.s.*** (mol %)			d.s.*** (mol %)			d.p.*										
	d.p.*			d.s.*** (mol %)			d.s.*** (mol %)										
1	1700	88	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
2	1700	88	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
3	1700	88	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
4	1700	98	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
5	1700	98	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
6	1700	98	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
7	600	88	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
8	1000	98	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
9	1700	88	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
10	1700	88	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
11	1700	88	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)
12	1700	88	Benzaldehyde (5)	Benzaldehyde (7)	Benzaldehyde (9)	Benzaldehyde (12)	Acetaldehyde (20)	Acetaldehyde (50)	Butyraldehyde (9)	Butyraldehyde (15)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)	Acetaldehyde (20)

* d.p. : Degree of polymerization ; ** d.s. : Degree of saponification ; *** d.s. : Degree of acetalization

[0072]

Because polyvinyl acetal resin (II) acetalized with acetaldehyde or butylaldehyde was not added in the Comparative Examples 1 and 2, the image was blurred in edge area. Thus, it showed poor ink absorbability. Because the polyvinyl acetal resin (I) was not acetalized with acetaldehyde or formaldehyde and polyvinyl acetal resin (II) acetalized with acetaldehyde or butylaldehyde was not added in the Comparative Examples 3 and 4, the image was very obscure in the edge area, showing poor ink absorbability. And, because the polyvinyl acetal resin (I) was not acetalized with aromatic aldehyde in Comparative Examples 5 – 8, the ink recording material showed poor water resistance. Thus, the recorded area dissolved and flowed off. And, because a fine powder of silicic acid or a fine powder of alumina was not added in the ink-accepting layer in Comparative Examples 9 – 12, the ink-accepting layer swelled and it showed bleeding of ink.

[0073]

In contrast, because the aqueous ink recording material obtained in Examples 1 – 12 contained polyvinyl acetal resin (I) that was prepared by acetalizing the polyvinyl alcohol with aromatic aldehyde and formaldehyde or acetaldehyde and polyvinyl acetal resin (II) that was prepared by acetalizing the polyvinyl alcohol with acetaldehyde or butylaldehyde and in addition they contained fine powder, the inks did not bleed in the image area. Thus, the image showed excellent clearness without blurriness around the image.

[0074]

[Effect of invention]

Because the aqueous ink recording material of this invention has the above-described constitution, it excels in water resistance and ink absorbability. Therefore, it hardly causes bleeding of inks, even when a color inkjet recording system that has a large amount of ink attachment is employed. Therefore, the aqueous ink recording material of this invention can be used for multicolor formation of record, for creation of fine dots, and for increasing the printing speed. Furthermore, because the aqueous ink recording material of this invention excels in transparency, it can be used appropriately in the sheet that allows observation of a recorded image using a transmission light, such as in OHP sheet and so on.